### **Tuesday Morning, November 3, 1998**

#### Surface Science Division Room 309 - Session SS2-TuM

#### **Noble Metal Catalysis**

Moderator: G.B. Fisher, General Motors R & D Center

8:20am SS2-TuM1 Microfabrication and Evaluation of Supported Model Catalysts, B. Kasemo, Chalmers University of Technology, Sweden INVITED Supported catalyst particles and single crystals exhibit differences in catalytic properties which are referred to as the structure gap in catalysis. Experimentally this is addressed by systematic studies of the influence of e.g. particle size and structure, and type of support on the catalytic properties. Modern microfabrication adds new opportunities, complementing the existing ones, to systematically manufacture and evaluate supported model catalysts. In this presentation the advantages and limitations of different microfabrication techniques are briefly reviewed. The use of electron beam lithography (EBL) applied to model catalyst production is described in detail. Specific examples are given of EBL manufactured noble metal catalysts on different supports. Evaluation of these catalysts in catalytic reactions involve (i) studies of morphological changes of the native structures caused by the reaction conditions and (ii) evaluation of the kinetics.

#### 9:00am SS2-TuM3 Chemisorption and Kinetic Studies of Model Low-Temperature CO Oxidation Catalysts: Au/TiO@sub 2@(110), V.A. Bondzie, S.C. Parker, C.T. Campbell, University of Washington

As a room-temperature CO oxidation catalyst, Au/TiO@sub 2@ shows exciting potential in automotive applications. Oxygen does not dissociatively adsorb on bulk Au, although one of the elementary steps in the proposed mechanism for this reaction is the activation of O@sub 2@ at the Au/TiO@sub 2@ interface. No such adsorption sites that react with molecular O@sub 2@ have so far been identified spectroscopically. In order to understand this reaction at the molecular level, O@sub 2@ chemisorption and CO titration over O-covered 2D and 3D Au islands, grown on TiO@sub 2@(110) have been studied. Techniques used included TPD, LEED, XPS and LEIS. A hot filament was used to deposit O adatoms. Subsequent TPD shows O@sub 2@ desorption with a peak maximum shifting from ~650 K (for 2-atom thick Au islands) to ~550 K (for bulk Au). No O@sub 2@ desorption is seen from 2D (i.e., 1-atom thick) Au islands below 770 K. This indicates that as the thickness of the Au islands decreases, the O adatoms bind increasingly strongly to the Au. The kinetics of the titration of oxygen adatoms with CO (CO@sub g@+O@sub a@ ? CO@sub 2,g@) were also measured from O-covered Au particles on TiO@sub 2@(110). The reaction rate on 2D Au islands is slower than on the 3D Au islands, even though CO bonds slightly more strongly on the former. This reflects a higher activation barrier on the 2D Au islands than on the 3D Au islands for the Langmuir-Hinshelwood step (i.e., CO@sub a@+O@sub a@ ? CO@sub 2,g@). This is due to the stronger O-Au chemisorption bond strength on 2D Au islands than on 3D islands. This stronger bond should promote dissociative O@sub 2@ adsorption, which we postulate as the rate-determining step in catalysis.

## 9:20am SS2-TuM4 Monte Carlo Simulations of Catalytic Reactions on Nanometer-sized Particles, *H. Persson*, *P. Thormählen*, *V.P. Zhdanov*, *B. Kasemo*, Chalmers University of Technology, Sweden

Using a Monte Carlo algorithm, we have investigated the 2A+B@sub 2@ @>=@ 2AB reaction both on a nanometer-sized catalyst particle, with interacting facets, and also on an infinite surface, which represents a macroscopic catalyst surface. The reaction mimics practically important catalytic processes such as CO oxidation on Pt, Rh or Pd. In the present work we have studied the role of diffusion between different facets, different reaction to diffusion rates and the effect of desorption in these systems. Our results indicate that the kinetics on nanometer-sized particles can be remarkably different compared to the kinetics on a macroscopic catalyst surface.

#### 9:40am SS2-TuM5 Ab Initio Density-Functional Theory Study of CO Oxidation Over Ru(0001), C. Stampfl, M. Scheffler, Fritz-Haber-Institut der MPG, Germany

Under "Realistic conditions" the rate of oxidizing catalytic reactions is very much higher at ruthenium than at any other transition metal, and the dependence on the oxygen partial pressure is qualitatively different.@footnote 1@ Yet, under ultra high vacuum (UHV) conditions Ru is by far the worst catalyst, and the question was frequently raised

concerning the relevance of Surface Science studies for real catalysis. Using density-functional theory we show in this contribution that the above noted "pressure gap" phenomenon is only apparent. Thus, if understood, it can be circumvented. In particular, we investigate both a scattering reaction of CO at the O-covered surface [Eley-Rideal mechanism (E-R)]@footnote 2@ and the Langmuir-Hinshelwood (L-H) reaction. In each case the transition state corresponds to a bent CO@sub 2@-complex with an associated bond angle of 131° (E-R) and 125° (L-H). The metastability of a carbonate species is also identified which could act as an intermediory species for CO@sub 2@ production. We attribute the enhanced CO@sub 2@ formation rate at elevated gas pressures (and high coverage) to be due to the notably weaker O-Ru bond strength compared to that at lower Ocoverages as are present under UHV conditions. In this respect we also report results investigating the affect of subsurface oxygen on the energetics of the reaction. Subsurface O has been proposed to be responsible for the very recently reported CO@sub 2@ reaction rates@footnote 3@ that are two orders of magnitude higher than those measured in Ref. 1. @FootnoteText@ @footnote 1@C. H. F. Peden and D. W. Goodman, J. Phys. Chem. 90, 1360 (1986). @footnote 2@C. Stampfl and M. Scheffler, Phys. Rev. Lett. 78, 1500 (1997). @footnote 3@A. Böttcher, H. Niehus, S. Schwegmann, H. Over, and G. Ertl, J. Phys. Chem. 101, 11185 (1997)

# 10:00am SS2-TuM6 The Effect of Strain on the Reactivity of Metal Surfaces, *M. Mavrikakis*, Technical University of Denmark, DENMARK; *B. Hammer*, Aalborg University, Denmark; *J.K. Norskov*, Technical University of Denmark, DENMARK

Self-consistent density functional calculations for the adsorption of O and CO, and the barrier to CO dissociation on strained and unstrained Ru(0001) surfaces are used to illustrate the general phenomenon of strained metal surfaces having chemical properties drastically different from those of unstrained surfaces. Surface reactivity increases with lattice expansion, following a concurrent upshift of the metal d-states. Consequences for the catalytic activity of thin metal overlayers are discussed.

#### 10:20am SS2-TuM7 In-situ Investigation of the Catalytic Reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@O on Pt(111) with Second Harmonic Generation, *F. Gudmundson*, Chalmers University of Technology, Sweden; *F. Eisert*, University of Heidelberg, Germany; *A. Rosén*, Chalmers University of Technology, Sweden

Most knowledge about catalytic reactions is obtained by the use of surface analytical tools, which are restricted to ultrahigh vacuum conditions. The extrapolation to real reaction conditions at ambient pressure however is connected with a relatively high uncertainty. Nonlinear optical techniques like Second Harmonic Generation (SHG) combine the capability of in-situ investigations with an inherent surface sensitivity. We present in-situ SHG investigations of the catalytic reaction 2 H@sub 2@ + O @sub 2@ @>=@ 2 H@sub 2@ O on Pt(111) in the pressure range between 200 mtorr and 10 torr at a catalyst temperature of T=700 K. With SHG the oxygen coverage is determined as function of the hydrogen partial pressure. In the pressure range investigated, the gas flow changes from molecular flow to laminar flow. This transition has a profound influence on the experimental observed oxygen coverages. However, using a kinetic reaction model of the hydrogen oxidation developed by Hellsing, Kasemo and Zhdanov the experimental results can readily be interpreted, if the transition of the gas flow conditions from molecular to laminar flow is taken into account.

#### 10:40am **SS2-TuM8 Suppression of Water Formation by Adsorbed Gold on Pt(335)**, *D.C. Skelton*, Michigan State University/General Motors R & D Center; *R.G. Tobin*, Tufts University; *D.K. Lambert*, *C.L. DiMaggio*, *G.B. Fisher*, General Motors R & D Center

Platinum, an excellent catalyst for water formation, has its catalytic activity significantly reduced by a submonolayer coverage of gold. As part of a larger study on surface reactions on modified electrodes for chemical gas sensors, temperature programmed reaction on a stepped platinum surface, Pt(335), at three gold coverages was studied. Reactive surfaces were prepared in UHV with systematic doses of hydrogen and oxygen to obtain submonolayer coverages of adsorbed atomic hydrogen and oxygen. Gold coverage was measured by comparing the relative intensities of the 64 and 69 eV Auger peaks of platinum and gold, respectively. At low coverages gold adsorbs into the step sites on Pt(335) [4(111)  $\times$  (100) in terrace step notation] and fills in to form islands which merge into a semi-continuous surface with openings to the platinum approximately 50 to 100 @Ao@ in diameter at 0.7 monolayers. This presumably leaves 30% of the surface platinum atoms available for chemisorption. However, hydrogen and oxygen in adsorption are reduced to 15% and 9% of their values on bare

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Pt(335), respectively, and bonding in step sites is reduced to 3% and 6%, respectively. Neither molecule bonds to the gold covered areas. The temperature-programmed reaction data for both Pt(335) and 0.7Au/Pt(335) show that this reduction in reactant coverage accounts for only part of the reduction in water production. Blockage of step sites by gold eliminates a major low-temperature reaction pathway seen on Pt(335) and a slight reduction in the desorption temperature of terrace hydrogen shifts hydrogen desorption into the same temperature range as water formation. At intermediate coverages (40% of the maximum hydrogen coverage and 50% of the maximum oxygen coverage) on each surface, the resulting competition between desorption and reaction lowers the reaction probability per hydrogen atom from 0.6 on Pt(335) to 0.2 on 0.7Au/Pt(335).

## 11:00am SS2-TuM9 Isothermal Kinetic Study of the Catalytic Reduction of Nitric Oxide over Rh(111) Surfaces, G. Chinnakonda, F. Zaera, University of California, Riverside

The kinetics of the thermal decomposition of NO and of its catalytic reduction to molecular nitrogen on Rh(111) surfaces was probed by isothermal measurements using an extension of the so-called King and Wells collimated beam method. Initial NO TPD studies corroborated previously reported results, including the development of two distinct molecular nitrogen desorption peaks at 460 and above 500 K, the first of which displays apparent first-order kinetics. In the isothermal experiments the rate of molecular nitrogen production was found to be significant above 450 K, and to be controlled by the recombination of atomic nitrogen below 600 K. In addition, the adsorption of NO was found to not be affected significantly by the presence of coadsorbed nitrogen and/or oxygen atoms at any temperature below 900 K. There is an induction period during which the surface concentrations of nitrogen and oxygen atoms build up before the recombination reaction starts. When performing the experiments with NO alone oxygen deposition on the surface eventually poisons the system and stops the reaction, but when using CO + NO mixed beams that oxygen is removed and a steady-state catalytic regime is reached. In any case, the experimental data could not be reproduced in a satisfactory manner by any empirical rate law unless the order in nitrogen coverage was set to less than unity, an observation that is interpreted here as being the result of the slow diffusion of nitrogen atoms across the surface prior to their recombination. A strong additional effect due to lateral repulsions between nitrogen and/or oxygen atoms was also observed.

# 11:20am SS2-TuM10 Surface Species and Desorption Products from NO Exposure on Clean and (Rh,Pt) Loaded Surfaces of Highly Oriented CeO@sub 2@ Characterized by SXPS and TPD, *S.H. Overbury*, *D.R. Mullins*, *D.R. Huntley*, Oak Ridge National Laboratory

Adsorption and reaction of NO on ceria, both with and without Rh or Pt additions, was studied by soft x-ray photoelectron spectroscopy and temperature programmed desorption. The results demonstrate the complexities and interactions which may occur in supported catalysts involving reducible substrates. Growth in UHV of thin films of CeO@sub 2@ on a Ru(0001) substrate allowed creation of oriented films with variable oxidation state, quantitatively determined by valence band and Ce 4d photoemission. Following NO exposure various N containing surface species were observed by N 1s photoemission, and their distribution depended upon surface oxidation state, exposure and adsorption temperature. These species included N@sub 2@O, NO, NO@super +@ and three states believed to be associated with NO@super -@ or atomic forms of N. Occurrence of adsorbed N@sub 2@O at 100 K indicates that NO dissociation and reaction occurs readily at low temperature. N@sub 2@ is evolved during adsorption from above 100 K to at least 600 K indicating that some NO direct decomposition occurs over a wide range of temperatures and coverages. Adsorption of NO at 150 K is predominantly molecular while exposure to NO at 400 K leads to a low binding energy atomic state which desorbs at temperatures above 500 K. NO adsorbed on oxidized ceria yields a molecular state at a higher binding energy than on reduced ceria and thus is associated with NO@super +@. Adsorption of NO on reduced ceria is oxidative resulting in strongly non-Langmuirian adsorption behavior. Deposition of Rh or Pt on these surfaces alters the observed NO chemistry, and the extent of reduction of the ceria in turn modulates the activity of the noble metal for NO dissociation. Greater dissociation probability of NO and increased stability of the resulting N atoms is observed for the noble metal deposited on a reduced compared to a fully oxidized support. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy

11:40am SS2-TuM11 An Investigation of the NO@sub x@ Storage Mechanism, M. Skoglundh, H. Persson, E. Fridell, P. Engström, S. Ljungström, Chalmers University of Technology, Sweden

In order to reduce nitrogen oxides (NO@sub x@) from lean burn vehicles, NO@sub x@ storage catalysts are used. The key idea is to first store NO@sub x@ in the catalysts during lean conditions (oxygen in excess) and then the NO@sub x@ is released and reduced during short periods of fuel rich conditions. In the present study we systematically investigate the sequence of mechanistic elementary steps in the NOx storage cycle, by using different experimental techniques in combination with theoretical modelling. As a model system we have used a NO@sub x@ storage catalyst containing Pt, @gamma@-Al@sub 2@O@sub 3@ and BaO as the storage component. Our results suggest that an intermediate peroxide step (BaO@sub 2@) is essential for storing NO@sub x@ as Ba(NO@sub 3@)@sub 2@. Furthermore, the relative importance of direct NO@sub x@ storage via gas phase or NO@sub x@ storage via Pt spillover is discussed.

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